The impacts of conifer harvesting on runoff water quality: a regional survey for Wales

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The impacts of conifer harvesting on runoff water quality: a regional survey for Wales

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Abstract

Major, minor and trace element chemistry of runoff at stormflow and baseflow from 67 catchments (2 to 5 ha in area) has been determined to investigate the effects of clear felling and replanting of conifers on stream water quality across Wales. Samples, collected by local forestry workers (Forest Enterprise staff) on a campaign basis on up to eight occasions, were for 16 mature first rotation standing forest: the remainder represented areas completely clear felled from less than one to up to forty years previously. As the waters drain acidic and acid sensitive soils, acidic runoff is often encountered. However, higher pH values with associated positive alkalinities and base cation enrichments are observed due to the influence of weathering reactions within the bedrock. There is little systematic variation in water quality between baseflow and stormflow for each site indicating a complex and erratic contribution of waters from the soil and underlying parent material. 80% or more of the data points show hardly any changes with felling time, but there are a few outlier points with much higher concentrations that provide important information on the processes operative. The clearest outlier felling response is for nitrate at five of the more recently felled sites on brown earth, gley and podzolic soil types. ANC, the prime indicator of stream acidity, shows a diverse response from both high to low outlier values (>+400 to −300 μEq/l). In parallel to nitrate, aluminium, potassium and barium concentrations are higher in waters sampled up to 4 years post felling, but the time series response is even less clear than that for nitrate. Cadmium, zinc and lead and lanthanides/actinides show large variations from site to site due to localized vein ore-mineralization in the underlying bedrock.

The survey provides a strong indication that forest harvesting can have marked local effects on some chemical components of runoff for the first four years after felling but that this is confined to a small number of sites where nitrate production and aluminium leaching are high. In general, deforestation leads to a reversal of acidification when the nitrate pulse is low. The variability in water quality from catchment to catchment is too high for generalized conclusions to be made over the extent of the potential changes from site to site. The value of an organised campaign of opportunistic sampling using an infrastructure of enthusiastic staff from regionally dispersed organisations associated with environmental matters (in this case the forestry industry) is highlighted.

Introduction

One of the main land-use changes in the uplands of the UK over the last 60 years has been the widespread introduction of exotic conifers in large, single-aged plantations (Hudson *et al.*, 1997). Many of these plantations are now reaching maturity so that extensive areas are about to be or are in the process of being felled and replanted. Much of the uplands has acidic and acid sensitive soils developed from base-poor parent materials and these have been impacted by acid deposition loadings (UKAWRG, 1988: Gee, 1990; Mason, 1990; UKRGAR, 1997). The introduction of conifers has added to the acid loading by increased scavenging of atmospheric pollutants (Fowler *et al.*, 1989) and the trees may have caused further acidification by removal of base cations into the growing biomass (Jenkins *et al.*, 1990). Now, with the onset of widespread felling, there is the potential for further acidification due to the generation of nitrate as biomass uptake is removed and rates of microbial mineralisation and nitrification are increased (Bormann and Likens, 1994). There have been several detailed catchment studies of deforestation effects on water quality and the results have shown variable acidification responses to felling; in some cases the acidity resulting from nitrate generation has effectively been neutralised by base cation release, in other cases it has not (Adamson *et al.*, 1987; Adamson and Hornung, 1990; Stevens and Hornung, 1987; Neal *et al.*, 1992a,b,c, 1887a, 1998; Bormann and Likens, 1994; Hornung *et al.*, 1994; Reynolds *et al.*, 1995). Indeed, in some cases the effects of felling has led to an increase in alkalinity (Neal *et al.*,

1998). There is now an urgent need to develop a regional strategy for assessing the range of hydrochemical responses to clear felling and replanting so that the vulnerability of sites can be assessed and appropriate management techniques developed.

Over the past five years, the Natural Environment Research Council in partnership with the Environment Agency and Forestry Commission have undertaken a study to address the issue of water quality change with harvesting and replanting based on two approaches. Firstly, paired-catchment experiments have been undertaken which focus on the initial one to two years following felling and replanting on upland soil types of particular concern (Neal *et al.*, 1998). Secondly, a regional survey of forested and harvested/replanted sites has been undertaken which covers a much larger timescale of felling and replanting as well as a broader range of site types. These approaches provide short (event to seasonal) and longer-term (yearly to decadal) perspectives of the ecosystem response to felling and growth of the second forest crop as well as giving insights into the dominant processes operative. In this paper, the first results of the regional survey are presented. The study compliments and provides a context for the analysis of data from paired catchment and associated studies (Neal, 1997e) and a much clearer representation of the wide variety of responses than hitherto seen. The combined approach is important to the development of appropriate process based environmental models to allow national assessment of water quality changes associated with UK upland forest plantation management.

Rationale, sampling strategy, study sites, and chemical analysis

RATIONALE AND SAMPLING STRATEGY

The rationale behind the regional sampling programme was to obtain soil and hillslope drainage 'endmember' chemistries representative of a variety of soil types in order to describe how the chemical composition of the major inputs to streamflow generation change with forest clearfell. The focus on soil drainage chemistry is justified because, under highflow conditions in the stream, when these inputs predominate, the main problems of stream acidity occur (Neal and Christophersen, 1989). Small discrete catchments were chosen (a) to provide an integrated measure of soil drainage water chemistry (very heterogeneous behaviour is observed at smaller scales such as within the soil pores; Neal, 1996) and (b) to minimise groundwater inputs which are more prevalent as baseflow discharge to the main streams. Drainage water samples were taken at both baseflow and highflow extremes so as to identify the range of responses. The regional extent of the survey and the intermittent nature of the hydrological extremes meant that an innovative campaign approach had to be used. This involved opportunistic high and low flow sampling by Forest Enterprise field staff. Sampling was 'triggered' at the Institute of Hydrology, Wallingford by central assessment of suitable weather patterns; then the sampling teams for each of the Forest Enterprise (FE) regions were alerted. The timing of low flow sampling was judged on the basis of dry weather conditions being maintained for a minimum of three weeks. High flow sampling was initiated to coincide with rainfall from particular frontal weather systems. It was left to the judgement of the field staff exactly when to sample, the criteria being that rainfall prior to the sampling was sufficient to 'wet up' the catchment fully and that flow from runoff had to be particularly high. Seasonality was incorporated into the experimental design: autumn storm flush and winter and spring stormflow periods were sampled as were spring, summer, autumn and winter baseflow periods. The campaigns covered the period autumn 1995 to spring 1998.

STUDY SITES

Of over 200 sample sites initially considered across Wales, a subset was selected to have (a) a catchment area between 2 to 5 ha, (b) a definable catchment boundary (c) a first order stream draining a single soil type and single site management regime, (d) available site information such as felling and replanting dates, (e) available FE staff for opportunistic sampling and (f) to be either fully forested or completely harvested (and in some cases replanted) at single stages in the past. By this process, 51 clear felled/replanted and 16 standing forest sites were selected from all the FE districts in Wales where representative catchments were available. The locations of the various sites and their identification numbering are provided in Appendix 1; Table 1 provides basic data on catchment attributes and Appendix 2 shows the regional distribution.

CHEMICAL ANALYSIS

Each field team was provided with appropriate cleaned glass and plastic bottles for sample collection. On sampling, the bottles were rinsed several times with stream water and filled bottles were returned to the local FE district office for dispatch on the same day to the Institute of Hydrology office at Plynlimon. At the start of the next

Table 1. A summary of data coverage for the catchments with differing soil types.

Soil type	Number of sites	Felling periods (years since fell)
Bog	8	0 to 5
Brown earth	10	0 to 9
Gley (PG)	32	0 to 9; 12 to 14; 47
Gley (SWG)	8	0 to 4; 14 to 16
Podzol (IIP)	8	0 to 9
Podzol (PIP)	9	0 to 7

working day, the samples were filtered through 0.45 μm membranes and stored in appropriate clean bottles for detailed chemical analysis. Gran alkalinities and pH were determined on unfiltered samples.

Two acidimetric titrations were performed for Gran Alkalinity (G-Alk), one to determine the effective bicarbonate buffering component (pH range 4.5 to 4.0: G-Alk1) and the other to determine both the bicarbonate and weak organic acid buffering components (pH range 4.0 to 3.0: G-Alk2). There are some differences between the two alkalinity measurements, but these are small compared to the large amount of temporal and spatial variation in the samples. Linear regression of the two determinations gives an r^2 of 0.995 (N = 387), a gradient not significantly different from unity (0.992 with standard error 0.004) and an intercept not significantly different from zero (1.0 with standard error 7.5). Consequently, in the remaining text only one of these values, G-Alk2, is used and this term is simply described as the 'alkalinity'.

The filtered samples were analysed at the Institute of Hydrology laboratories at Wallingford for major, minor, nutrient, trace and ultra-trace element analysis using a wide range of automated-colorimetric, spectrometric and ion-chromatographic techniques. Details of these procedures are provided in earlier publications (Neal *et al.*, 1992a, 1997).

Within the following text, reference is made to the primary measure of the net acidity of each water, the Acid Neutralization Capacity (ANC). This has been calculated from alkalinity, total dissolved aluminium (T-Al) and dissolved organic carbon (DOC) concentrations using the formula developed by Robson (1993):

$$ANC = \{G\text{-}Alk2\} - 3*[T\text{-}Al] + 0.054*[DOC]$$

where {} and [] refers to concentrations in μEq/l and μM/l units respectively.

Results

GENERAL FEATURES OF WATER QUALITY PATTERNS

Water quality across the region varies from acidic and aluminium bearing to circumneutral waters containing calcium with relatively high alkalinity and ANC values (Appendix 3 and Table 2). For example, pH varies between about 4 and 7.2 for both standing forest and felled

Table 2. A summary of the water quality of the forested and clearfelled survey sites. All the concentrations are expressed in Eq/l units except for pH which is dimensionless and DOC which is M/l.

Forested sites		Average	Median	Minimum	Maximum
Na	μEq/l	232.92	210.43	134.35	393.48
K	μEq/l	9.08	6.92	2.31	50.00
Ca	μEq/l	71.35	67.25	20.50	171.00
Mg	μEq/l	80.93	75.72	27.98	169.55
Al	μEq/l	32.32	25.18	2.74	104.96
SO_4	μEq/l	129.46	125.94	68.54	356.88
Cl	μEq/l	259.02	229.90	126.94	473.91
NO_3	μEq/l	36.23	29.44	0.00	216.13
pH		5.00	4.88	4.04	6.54
G-alk2	μEq/l	–5.34	–6.88	–90.45	96.02
ANC	μEq/l	–39.51	–40.34	–128.33	92.20
DOC	μM/l	209.42	125.00	0.00	975.00
Felled sites		**Average**	**Median**	**Minimum**	**Maximum**
Na	μEq/l	216.77	210.43	115.22	454.78
K	μEq/l	8.26	6.41	0.00	56.92
Ca	μEq/l	104.00	75.00	20.50	1460.00
Mg	μEq/l	83.16	74.90	27.98	476.54
Al	μEq/l	29.37	23.16	0.92	229.76
SO_4	μEq/l	132.21	128.75	56.67	436.67
Cl	μEq/l	231.84	222.85	107.19	499.29
NO_3	μEq/l	41.23	24.19	0.00	500.00
pH		5.35	5.03	4.07	7.18
G-alk2	μEq/l	25.21	–1.13	–89.46	1499.83
ANC	μEq/l	–5.14	–28.71	–305.08	1496.11
DOC	μM/l	228.12	150.00	0.00	1400.00

sites. Correspondingly, most ANC values lie in the range +200 to −200 μEq/l but there are also a few higher and lower values. For waters with particularly high ANCs (>+200 μEq/l), the main ions are (a) bicarbonate which is mainly balanced by base cations (calcium in particular) and (2) chloride which is mainly counterbalanced by sodium (Table 3). Under more acidic conditions where ANC values are particularly low (< −200 μEq/l), hydrogen-ions and, especially, aluminium become important to the cation charge: the balancing anions are sulphate, chloride and, particularly in the case of felled sites, nitrate. Under these acidic conditions, sodium and chloride are also major components of the charge balance and they approximately counterbalance each other (Table 3). Waters with intermediate ANCs have compositions which lie between these two extremes (Table 3): the neutralization of the more acidic drainage waters by groundwaters ensures linear features for the chemically conservative base cations, strong acid anions and ANC, but more complex behaviour for the non-conservative components such as bicarbonate and aluminium which are influenced by chemical processes across the pH range. Statistical analysis of the entire data reveals no significant difference across the regions or between stormflow and baseflow conditions. Further, a statistical analysis for all the individual sites separately is not appropriate given the limited number of collections for many sites. However, for the few sites with the most (6) samplings, statistical analysis reveals no significant difference between stormflow and baseflow conditions.

Table 3. An illustration of the chemical composition of three distinct water types within the survey: low ANC (site C41), near zero ANC (site A25) and high ANC (site B3).

	C41 μEq/l Cations	C41 % Cations	A25 μEq/l Cations	A25 % Cations	B3 μEq/l Cations	B3 % Cations
Na	208	29	129	50	203	30
K	57	8	2	1	4	1
Ca	66	9	55	21	363	54
Mg	108	15	51	20	97	15
Al	230	32	17	7	3	0
H	58	8	6	2	0	0
	Anions	Anions	Anions	Anions	Anions	Anions
NO_3	500	64	0	0	12	2
SO_4	104	13	76	29	119	18
Cl	152	20	147	56	178	27
HCO_3	0	0	21	8	357	53
DOC	23	3	16	6	5	1

WATER QUALITY PATTERNS: WITHIN AND ACROSS CATCHMENT VARIABILITY

There are clear site to site differences and these are illustrated in Figs. 1 to 3 where the mean and ranges in nitrate,

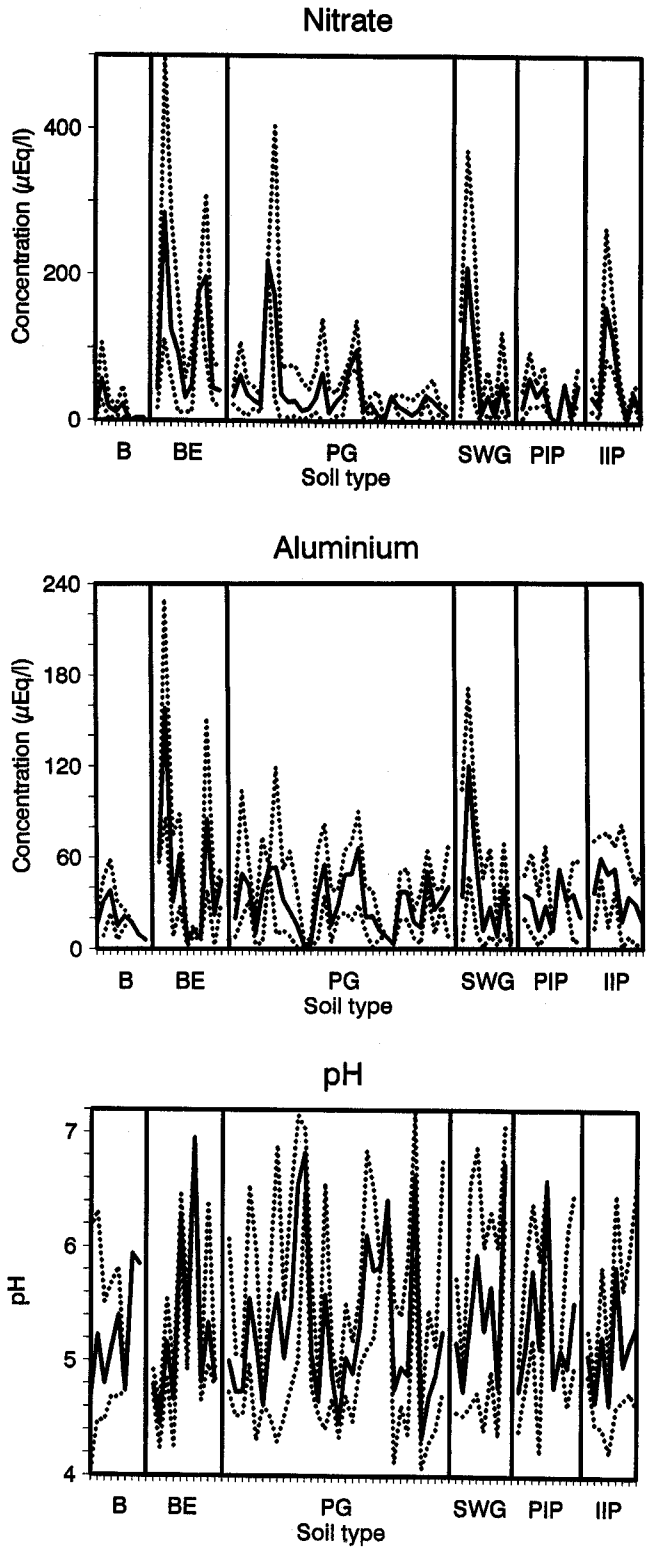
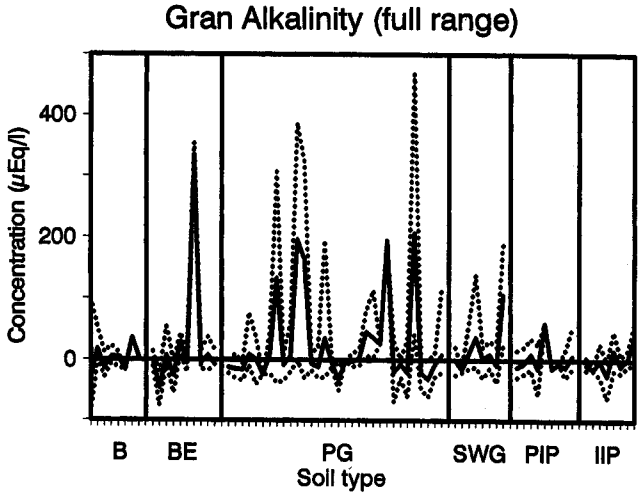
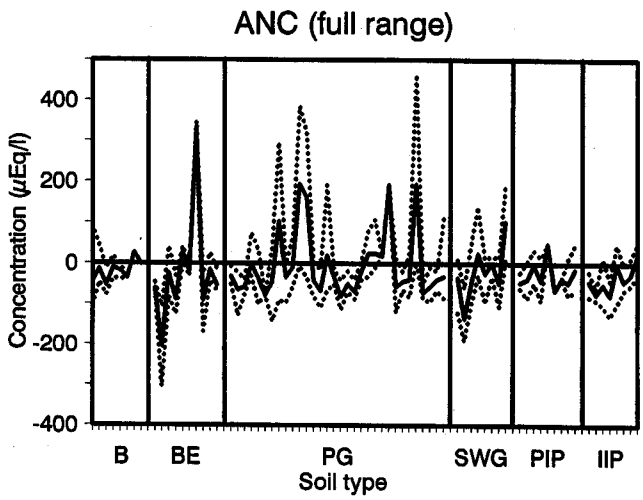
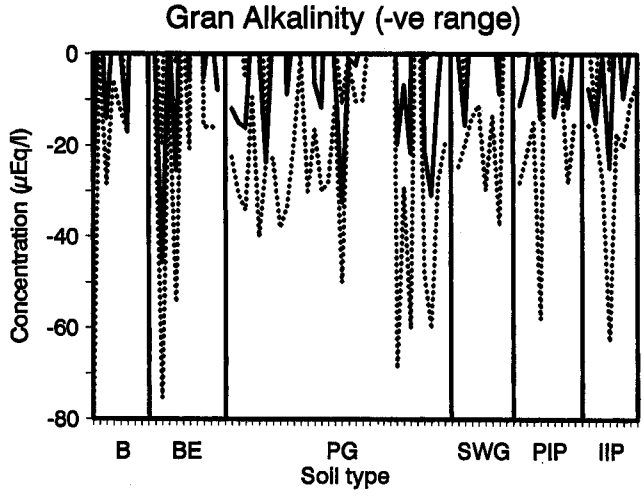


Fig. 1. *Variations in average, minima and maxima for nitrate and aluminium concentrations and pH across the survey sites.*







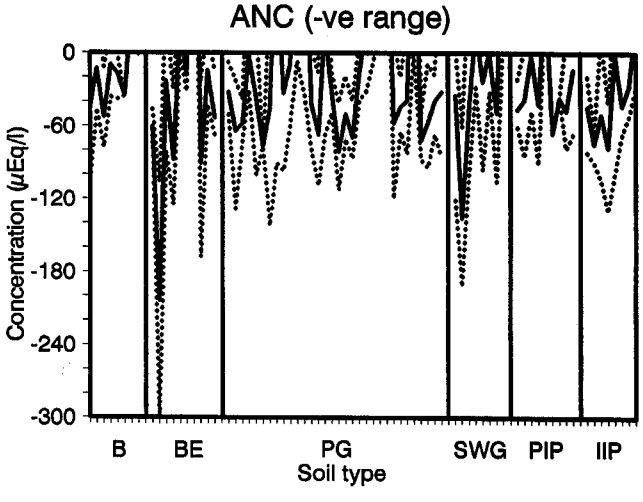


Fig. 2. *Variations in average, minima and maxima for Gran alkalinity across the survey sites. Two plots are provided, one covers the full range of concentrations while the other focuses in on the more acidic conditions where negative values occur. Note that at one brown earth site (the seventh point in the sequence), a very high value of Gran alkalinity (>1000 Eq/l) was observed which distorted the results: this point was not included in the plot and the computed average does not include this value.*

Fig. 3. *Variations in average, minima and maxima for ANC across the survey sites. Two plots are provided, one covers the full range of concentrations while the other focuses in on the more acidic conditions where negative values occur. Note that at one brown earth site (the seventh point in the sequence), a very high ANC value (>1000 Eq/l) was observed which distorted the results: this point was not included in the plot and the computed average does not include this value.*

aluminium, alkalinity and ANC concentration together with pH are plotted for the individual sites. In the diagrams, the sites are organized in a sequence of soils from left to right, bog (B), brown earth (BE), gley (PG, peaty gley; SWG, surface water gley) and podzol (PIP, peaty iron pan; IIP, intergrade iron pan). For each soil grouping, the sites are listed in a sequence left to right of increasing time between felling and sampling. The dashed lines represent the minimum and maximum values and the solid line the average. There are two points to note in the light of the variation in the number of samples collected at each site. Firstly, a very limited number of samples has been taken: indeed some sites are represented by only one sample and hence the minimum, maximum and mean values are the same. Clearly, the plots do not reflect the full range of variability. Secondly, the plotted sequence of time between felling and sampling is an average in some cases (eg, the sampling period can cover up to two years). More detailed assessment of the influence of felling age comes later in this paper when individual points are plotted.

The chemistry of the individual catchments is very variable and no site can be classed as being of fixed composition. In terms of stream acidity, all the catchments show a wide range of values for indices such as pH, alkalinity and ANC. Considering ANC in more detail, the brown earth and peaty gley sites show the largest fluctuations. One

brown earth site has a particularly high average ANC (>300 μEq/l) whilst another has a particularly low average ANC (<–180 μEq/l). The range in average values for the peaty gley sites is lower, but the spread in values for individual sites can be large due to the influence of waters with ANCs>100 μEq/l. Indeed, for about a fifth of the gley sites, average ANC is positive. For the other soil types, these extremes are not observed although there are fluctuations in ANC of over 50 μEq/l. There is also a large range in nitrate concentration from site to site, and particularly high values (mean concentration >100 μEq/l and maximum concentrations > 250 μEq/l) occur at four of the ten brown earth sites, three of the 40 gleys (1 PG and 1 SWG) and one of the 17 podzol (IIP) sites. These high values are observed at sites where felling occurred within four years prior to sample collection. There are also large site to site differences in aluminium concentration. Relatively high average (>80 μEq/l) and maximum (>100 μEq/l) aluminium concentrations are observed at two brown earth and one surface water gley site where the high nitrate concentrations occur.

WATER QUALITY VARIABILITY: LINKAGES WITH TIME SINCE FELLING

In order to establish patterns of water quality change with felling, a simple data interrogation scheme was introduced where determinand concentrations were plotted against time between felling and sampling using data-labels corresponding to the different soil types. For many of the determinands, the data broadly show two main features with time since felling. Firstly, for over 80% of the post felling samples, concentrations are within the range observed for the standing forest sites and, given the scatter to the data, trends are absent or very poorly defined for this main data swarm. Secondly, concentrations are much higher for the remaining samples. Further, even for the periods since felling where high concentrations occur, they constitute only a fraction (often <50%) of the total number of samples taken during that time. These two patterns become clearer when the frequency of concentrations is compared for different time since felling bands. This is illustrated for nitrate in Table 4.

For the majority of samples, the analysis cannot be taken further because of the confounding nature of the interactions between distribution of soil types, flow regime etc. For example, examination of the time series data for two key water quality indices, nitrate and ANC (Fig. 4) shows the following.

Bog soils. There is no clear pattern with time since felling and all values lie within the range of the standing forest. However, the key period of 0.5–3 years post-felling has not been sampled.

Brown earths. A clear nitrate signal is observed between 0.5 and 3 years after felling but most values fall within the range corresponding to standing forest sites. However, years 5 and 6 post-felling are missing. For ANC the data are highly scattered although there are some high and low values during the first three years after felling. A much more extensive data set is required to clarify the response.

Podzols and gleys. These show similar features and cover a wide time span in relation to felling. The data show a combination of responses for nitrate which broadly fit into three patterns: (a) the majority of points have low nitrate concentrations irrespective of time since felling, (b) a decline with time since felling in the maxima for the higher density data swarm and (c) anomalous peak 0.5 to three years following felling. This feature is illustrated in Table 4 where nitrate frequencies are presented for the entire dataset: the podzols and gleys constitute the majority of the data. For ANC, there is no clear pattern at all.

The high concentration outliers, which fall into four groups of determinands, have been investigated further:

Nitrate, aluminium, potassium and barium. The highest concentrations were observed during the first 2–4 years since felling at a few sites associated mainly with brown earth soils but other acid soil types were also represented (Figs. 4, 5). For example, there are fourteen data points where nitrate concentrations exceed 160 μEq/l (10 mg-NO_3/l). These represent 10 locations (A29, A48, B37, B38, B39, B40, B62, B63, C41, D42, and E45) and includes about a third of the total number of data points for these sites. Correspondingly, there were 8 relatively high values for aluminium (four sites: A29, B40, C41, E45) and potassium (four sites: A50, B39, B60, C41). The higher barium values were mainly for one site (NA48).

Calcium, alkalinity and ANC. These show a varied response (Figs. 4, 6). However, in the case of alkalinity and ANC, low values (<–50 and <–100 μEq/l, respectively) occurred during the first four years after felling. Within this time span, sites draining brown earth soils covered a wide range of ANC and alkalinity response. For both alkalinity and ANC, there were eight samples with relatively high values (>300 and >200 μEq/l, respectively). However, about 70% of all the data points had negative values for alkalinity and ANC and there were about 11 outliers with values of <–50 and <–100 μEq/l, respectively. For example, two brown earth sites had consistently low ANC values (A29 and C41; three data points at each site), while three gley sites (B40, 2 out of 3 points; A51, 1 out of 7 points; D43, 1 out of 2 points) and one podzol site (B37, 1 out of 3 points) had high values for part of the period.

Iron, manganese and DOC. Elevated concentrations were observed during the ten year period following felling at some of the 32 sites on peaty gley soils (Fig. 6): four had iron concentrations >10 μEq/l, eight had manganese concentrations >6 μEq/l, and six had DOC concentrations

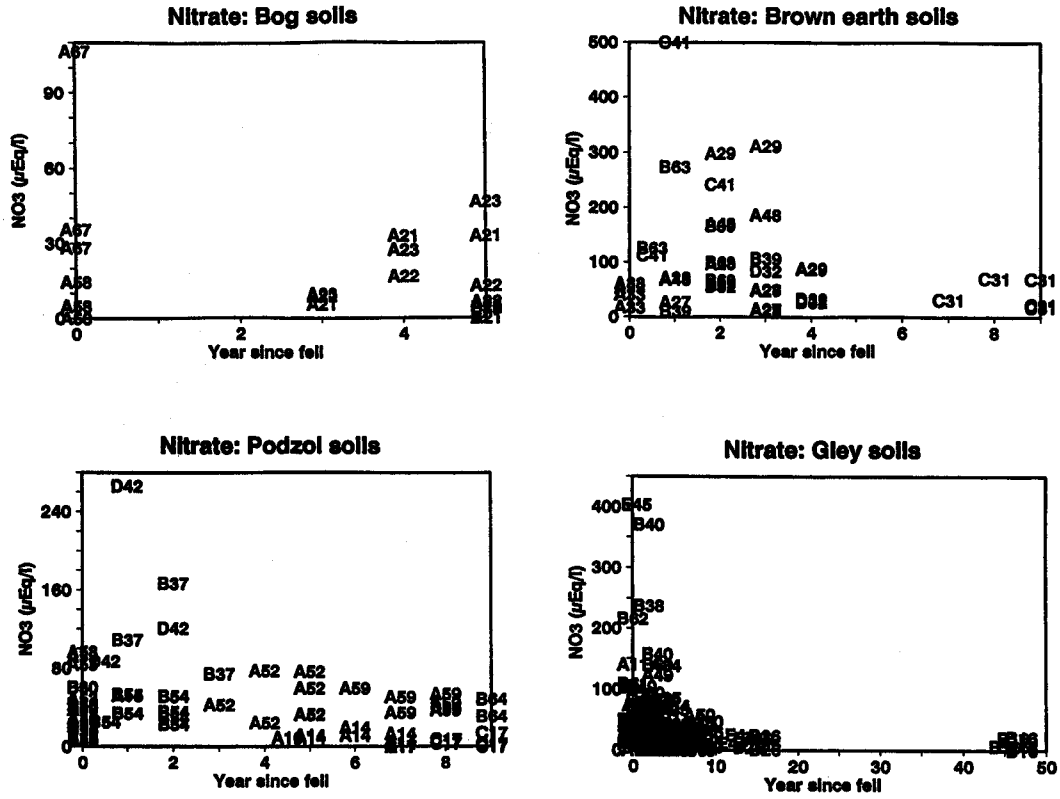


Fig. 4a. *The variations in nitrate concentrations with time since fell for the main soil groupings.*

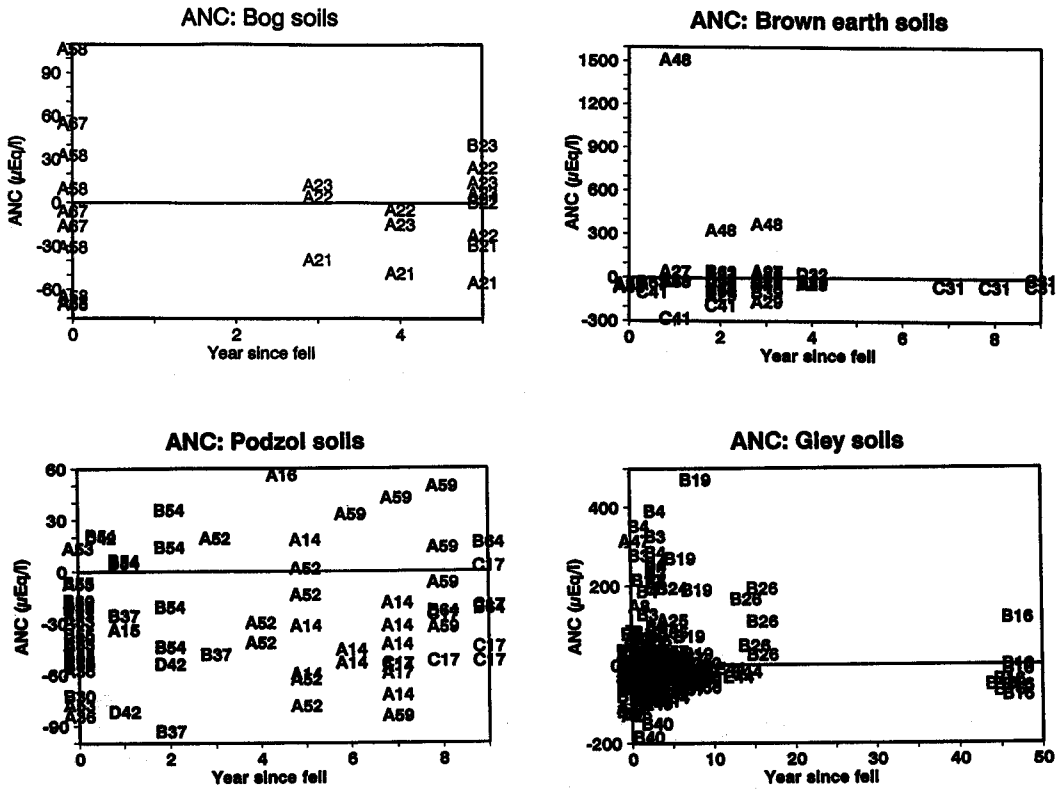


Fig. 4b. *The variations in ANC with time since fell for the main soil groupings.*

Table 4. Frequency distribution of nitrate concentrations with time since felling for the regional survey data.

NO_3 (Eq/l)	Year 0	Year .5–2	Year 3–4	Year 5–6	Year 7–8	Year 9–16	Year 47
0	6	2	4	13	11	12	11
10	8	9	30	28	32	16	44
20	16	12	18	15	13	28	11
30	20	21	12	10	3	28	22
40	14	6	6	15	21	4	11
50	20	7	9	5	11	8	0
60	2	9	1	5	8	0	0
70	3	6	0	3	0	4	0
80	1	4	5	5	3	0	0
90	1	2	6	0	0	0	0
100	2	3	0	0	0	0	0
110	3	2	1	0	0	0	0
120	0	2	0	0	0	0	0
130	0	2	2	0	0	0	0
140	0	0	1	0	0	0	0
150	1	0	1	0	0	0	0
160	0	0	1	0	0	0	0
170	0	3	0	0	0	0	0
180	0	0	0	0	0	0	0
190	0	0	1	0	0	0	0
>190	1	9	1	0	0	0	0

>900 μM/l on at least half of the sampling occasions. It appears that the more mature second rotation sites are on peaty gley soils. For this reason, it is not clear that any inferences can be drawn over whether or not the patterns relate to felling, soil type or a combination of both.

Trace elements. At four sites, there are anomalously high values for several trace elements. Two types of pattern emerge in this category. Firstly, cadmium, zinc and lead are all enriched for one peaty iron pan site (CB54). Here, concentrations reach values of about 6, 1800 and 70 μg/l, respectively, against corresponding background levels of <0.5, <100, and <2 μg/l. Secondly, there is enrichment in some lanthanides and actinides together with yttrium and uranium (and possibly nickel) at three sites (LA13, LA14 and LA27) which have peaty gley and intergrade iron pan soils. The high values and corresponding background values (presented in brackets) are; La, 3.2 (1.0); Pr, 0.8 (0.2); Ce, 13 (2); Y, 3.0 (<0.6); U 0.16 (<0.03 μg/l); Fig. 7. There are a further two sites where lanthanum and praseodymium are also enriched (LA2 and LB5). It is not clear if the patterns observed for either group of sites correspond to felling activities. However, in both cases, the sites are in areas with known vein ore-mineralization and this, rather than felling, is likely to be the primary factor.

IDENTIFYING CONCENTRATION INTERRELATIONSHIPS ASSOCIATED WITH FELLING: GRAPHICAL AND STATISTICAL APPROACHES

The concentrations of those determinands which showed changes with felling age were plotted against nitrate, the primary strong acid anion response with felling, to identify underlying patterns (Figs. 8, 9). Two main patterns emerged. Firstly, plots of aluminium, potassium and barium against nitrate gave positive relationships but with high data scatter. Two linear features were observed for barium: (a) a steep barium to nitrate gradient is mainly for one brown earth site, (NA48), although a peaty gley site, (DA24), is also represented and (b) a shallow barium to nitrate gradient occurs for a series of observations and a range of sites. A more complex relationship was identified between nitrate, alkalinity and ANC. At intermediate to high nitrate concentrations, both alkalinity and ANC had negative values: in the case of ANC an approximately linear and negative relationship occurred but with high data scatter. At low nitrate concentrations, no pattern emerged other than the alkalinity and ANC both had mainly positive values and these values were either near-to or well-above the nitrate trend line observed at higher nitrate concentrations.

The high degree of inter-element scatter results from a complex series of hydrological and hydrochemical reac-

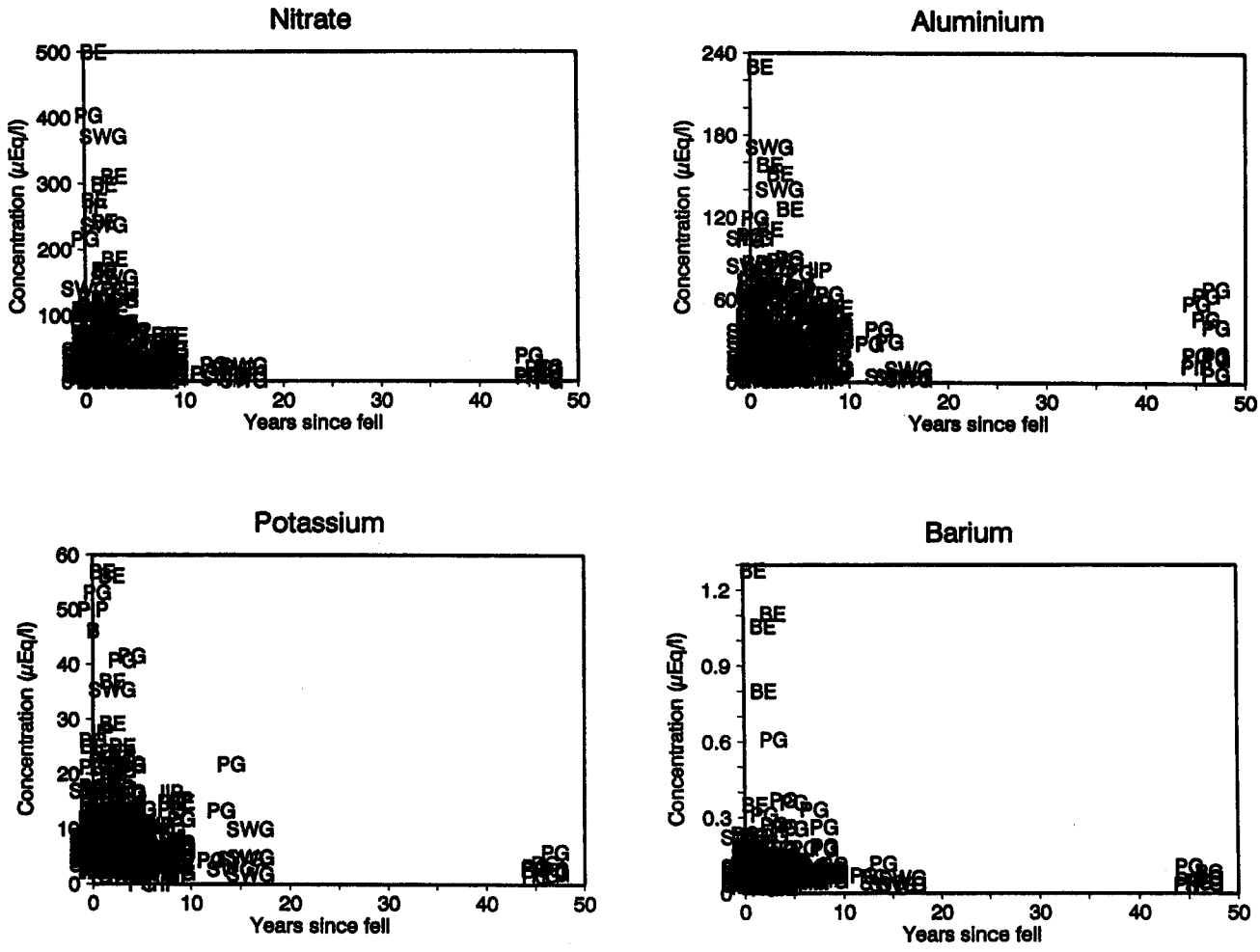


Fig. 5. *The variations in nitrate, aluminium, potassium and barium against time since fell.*

tions. Within a companion paper, the value of a multiple regression approach for identifying key hydrochemical processes is shown (Neal *et al.*, 1998). From acidification theory (Reuss and Johnson, 1986), changes in nitrate, chloride and sulphate are accompanied by parallel changes in calcium and aluminium and opposite changes in alkalinity and ANC (here termed acidification indices, AI). However, the regional behaviour will be far more complex than for individual catchments owing to the confounding influence of variable weathering rates, cation exchange stores and cation exchange selectivity coefficients in the soils (Neal, 1996) and variable weathering rates in the shallow groundwaters (Neal *et al.*, 1997b,c,d; Hill and Neal, 1997). To examine the influence of these major anions on stream acidity, a linear multiple regression analysis has been performed using lithium and silica as surrogates for weathering controls which counterbalance the acidifying effects of increasing strong acid anion concentrations. Lithium and silica were chosen on the basis of data from Plynlimon which show that these elements are derived almost exclusively from within-catchment sources; the inverse relationships observed with flow indicate an essentially bedrock weathering source (Neal *et al.*, 1997a). The regression equation takes the form:-

$$a*[Li] + b*\{Si\} + c*[SO_4] + d*[NO_3] + e*[Cl] + f = [AI]$$

where a, b, c, d and e are the regression coefficients, f is the regression constant and [] and {} refer, as earlier, to concentrations in μEq/l and μM/l units, respectively. As there were very contrasting situations with both alkaline and acidic waters involved, the analysis was undertaken for these distinct water types (the data being divided on the basis of ANC=0) and for the full dataset to see if there were clear differences corresponding to contrasting hydrochemical provenance. The regressions for the full and ANC<0 and ANC>0 datasets provide respective r^2 values of 0.39 (N=390), 0.45 (N=285) and 0.49 (N=105) which are highly significant statistically ($p<0.01$). The coefficients obtained for sulphate and nitrate with aluminium, alkalinity, ANC and calcium are shown in Fig. 10. In the case of chloride, no statistically significant coefficients were obtained for any of the AIs for the ANC<0 and ANC>0

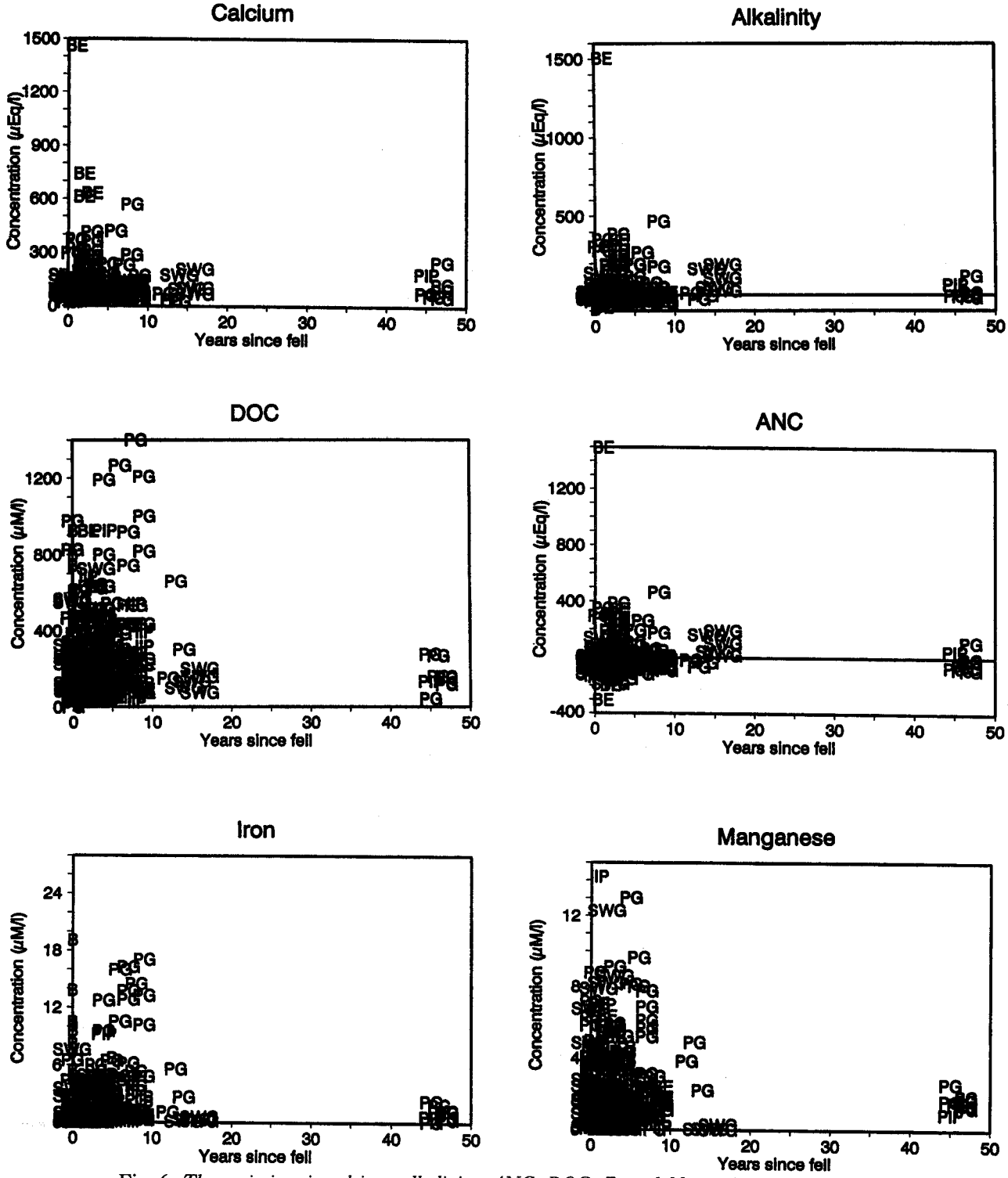


Fig. 6. *The variations in calcium, alkalinity, ANC, DOC, Fe and Mn against time since fell.*

data sets, possibly due to the relatively small ranges in concentration. However, for the full dataset, a statistically significant relationship with ANC was observed with a regression coefficient of –0.22 µEq-ANC/µEq-Cl: because of this lack of a clear pattern, little further comment is made for this anion in the remaining text.

Sulphate: There are clear, statistically significant positive relationships for alkalinity, ANC and calcium for the full and the positive ANC datasets, but no statistically significant results for the ANC<0 dataset other than with calcium. The overriding control of sulphate on these three AIs is one of weathering of the bedrock which leads to

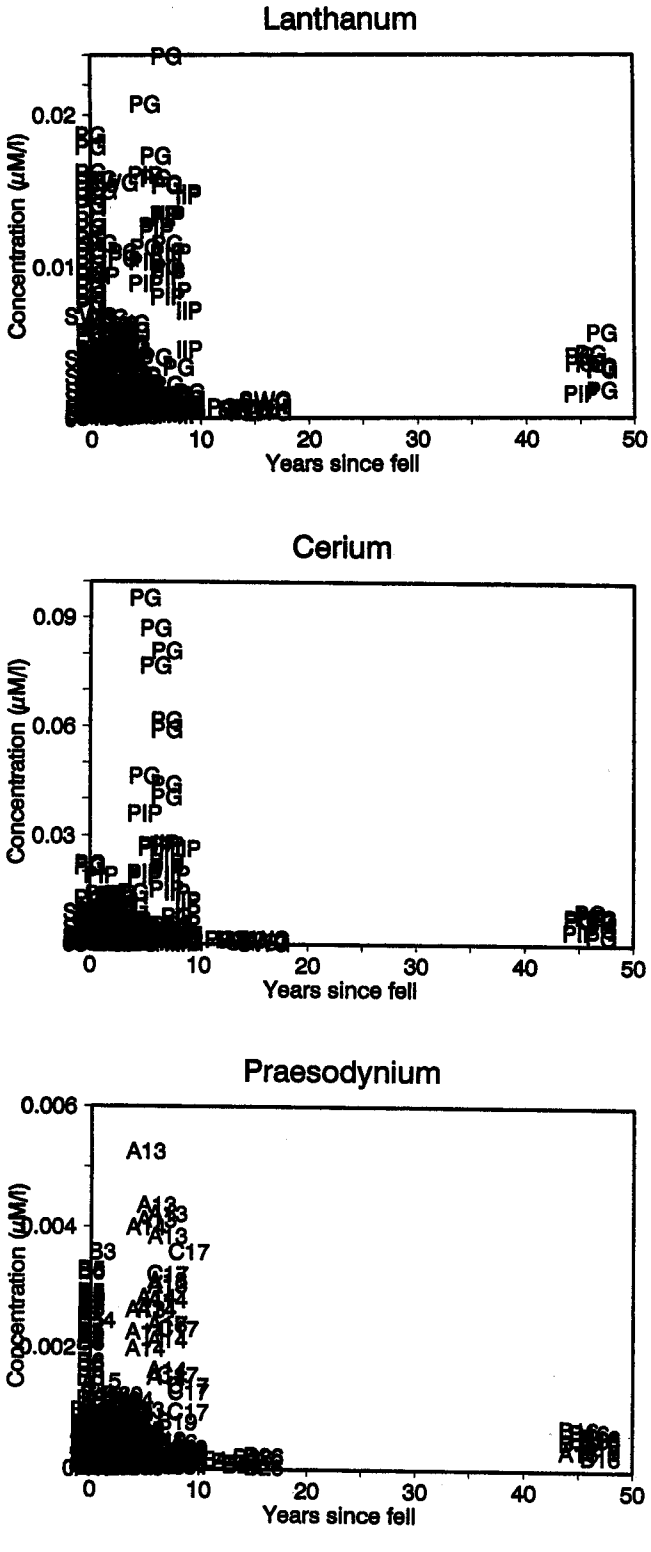


Fig. 7. *The variations in lanthanum, praesodymium, cerium, lead, zinc and cadmium against time since fell.*

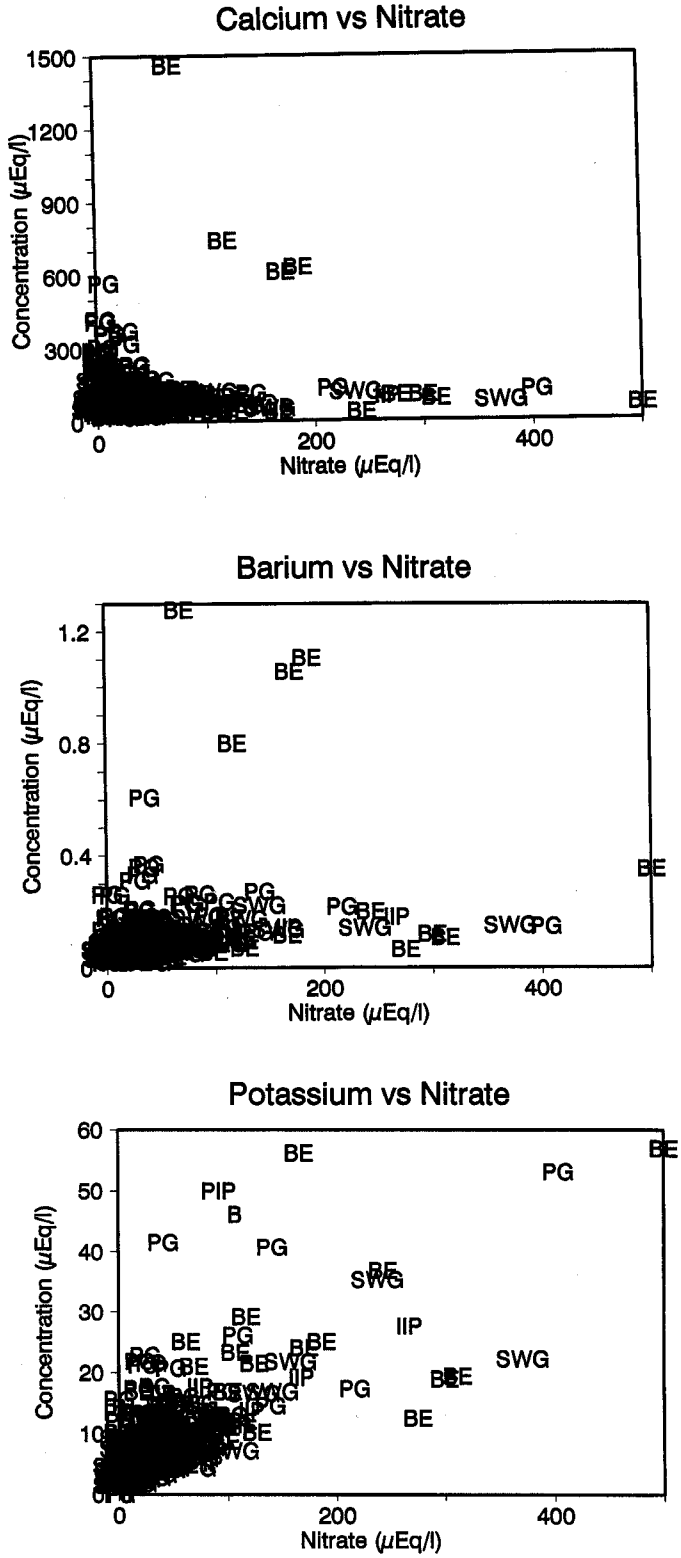


Fig. 8. *Plots of the concentrations of calcium, barium and potassium against nitrate.*

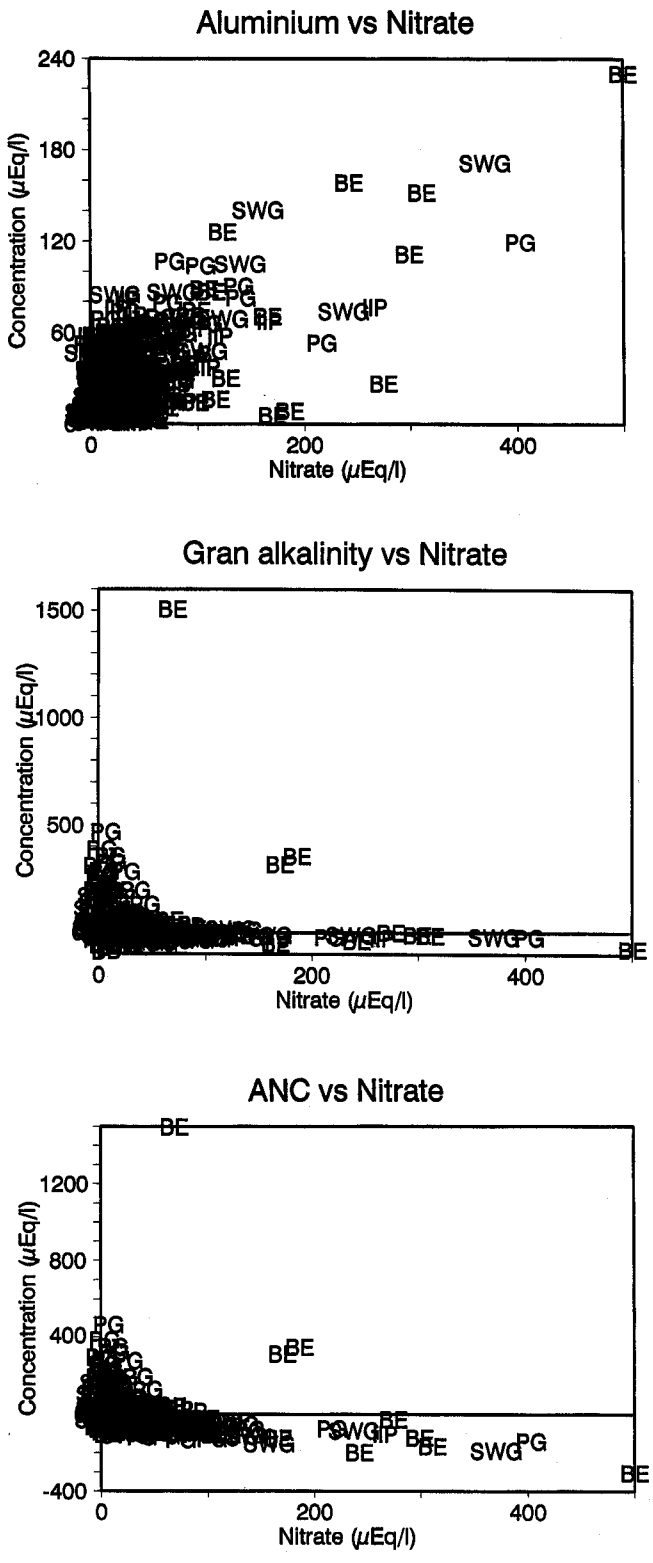


Fig. 9. *Plots of the concentrations of aluminium, alkalinity, and ANC against nitrate.*

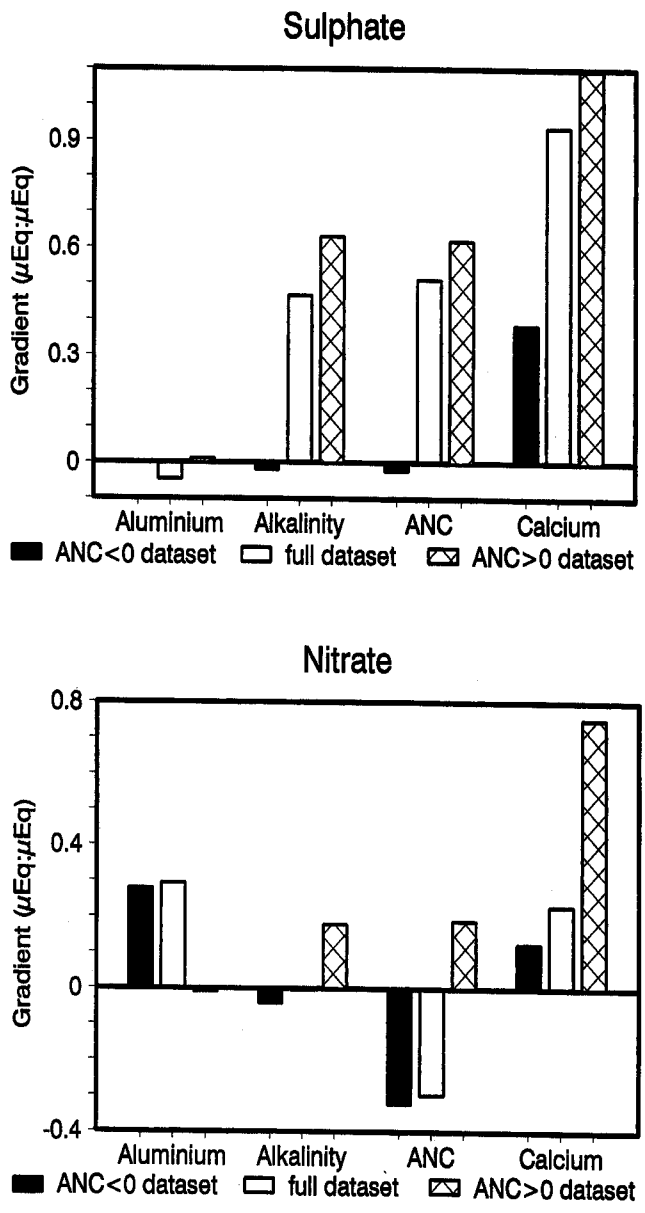


Fig. 10. *Plots of average regression coefficients for aluminium, alkalinity, ANC and calcium against sulphate and nitrate.*

parallel increases in calcium and bicarbonate (as expressed as a positive term for alkalinity and ANC): cation exchange should give a negative relationship. There is no statistically significant effect for aluminium. At ANCs>0, more alkaline conditions pertain and aluminium would not be an important component in solution owing to aluminium hydroxide solubility controls (cf. Neal and Christophersen, 1989) while at low ANCs, sulphate concentration variations are sufficiently small to negate statistical identification of a cation exchange mechanism.

Nitrate: There are statistically significant relationships for aluminium, calcium and ANC for the ANC<0 and the full

datasets. In the case of aluminium, the relationship is a positive one, while for ANC, it is negative to the same degree as aluminium is positive. In contrast, alkalinity does not show a corresponding change to ANC. This pattern is consistent with increased acidity associated with nitrate generation being linked to aluminium solution (with concomitant ANC decline) and increased calcium. For the positive ANC data set, as nitrate varies alkalinity, ANC and calcium show corresponding changes. While this pattern is consistent with cation exchange theory for calcium, it is incompatible with theory for alkalinity and ANC. However, with nitrate generation and organic matter decomposition, carbon dioxide is also generated. This, in turn, will cause increased base cation weathering under less acidic to alkaline conditions and the promotion of bicarbonate generation within the water. It is probably this process which gives rise to the anomalous result.

Discussion

The survey results suggest that an alkaline groundwater component seems to be present even at the small catchment/hillslope scale. Thus, runoff chemistry is less acidic than might be expected from the analysis of waters directly extracted from the soil. This is consistent with the more recent findings at the Plynlimon catchments (Neal *et al.*, 1997b, 1998; Hill and Neal, 1997); they show, conclusively, show a general characteristic and not simply a local anomaly. The results confirm that there is a high degree of variability in the chemistry of runoff from catchments draining apparently similar bedrock and soil types. Further, the results show that it is difficult to predict where groundwater will or will not provide an important source of alkaline inputs to either drainage waters or streams. For example, alkaline waters are observed at acid peaty gley sites even though, intuitively, such an input would not be expected due to the supposedly impermeable nature of the lower soils. Further, more extreme high and low acidity waters occur at sites with more freely drained brown earth soils. In this case, it is extremely difficult to predict whether acid or alkaline conditions will prevail or even what an average case might be.

The results provide important clues to the importance of particular processes of which groundwater inputs is only one. For example, changes in ANC within catchments and associated runoff are linked to strong acid anion variations (nitrate, sulphate and chloride). Increases in any of these strong acid anions without a balancing increase from base cation weathering lead to increases in soil water acidity (Reuss and Johnson, 1986). Similarly, decreases in strong acid anions without compensating changes in base cation levels will lead to reduced acidity (Neal *et al.*, 1998). In the present study, the main strong acid anion change is nitrate, albeit at a restricted number of sites and a limited number of samples; chloride and sulphate show only small or non systematic variations in concentration across the sites. Thus, in its extreme, a nitrate pulse dominates the net strong acidification response to changing total strong acid anion concentrations. The multiple regression results show that increasing nitrate concentrations lead to aluminium release and ANC decline by about 0.3 μEq/μEq-NO_3, the remaining charge balance probably being linked to base cation release. This value is lower than that observed in a companion paper where a value of about 0.5 μEq/μEq-NO_3 was obtained. It seems that for the highly acidic sites monitored in the regional survey, greater nitrate production and acidity generation is taking place in the lower soils where aluminium is primarily available for leaching and cation exchange. In the case of sulphate, the positive link with alkalinity, ANC and calcium indicates the importance of sulphate weathering sources. Indeed, this result for sulphate may well have ramifications for long term acidification modelling associated with acidic deposition, where the sulphate weathering term is usually ignored and all sulphate is assigned to atmospheric sources.

With regards to the other determinands, the availability of certain trace metals such as cadmium, lead, zinc, actinides and lanthanides in the bedrock and iron, manganese and barium in the soils from particular localities within the region, does raise an issue of metals mobility. For the few detailed studies, such as at Plynlimon, where trace metal mobilization has been studied in upland areas, bedrock mineralization can lead to metal enrichment in the soils and release to the streams during highflow periods (Neal *et al.*, 1997a). However, at these sites there seems to be no deforestation effect either to enhance or reduce mobilization except in the case of barium concentrations (see below). In the case of iron and manganese, soil disturbance can lead to releases to the stream for example in relation to DOC generation which complexes and stabilizes these reactive metals in solution.

The results of this study indicate that in many cases there is an insignificant hydrochemical responses to felling. In exceptional cases, increased nitrate and potassium concentrations corresponding to those seen at several other sites are observed (Bormann and Likens, 1994; Hornung *et al.*, 1990; Reynolds *et al.*, 1995; Neal *et al.*, 1998): an increase in barium concentrations in drainage water with felling is in line with observations for an area in the Hafren Forest at Plynlimon, mid-Wales (Neal et al., 1992a,b,c, 1997). In the case of nitrate, preliminary examination of the site details of the survey catchments revealed that the few sites with nitrate concentrations exceeding 160 μEq/l (10 mg-NO_3/l) were those primarily where (a) replanting and natural revegetation of the ground had not occurred following felling and/or (b) early autumn storm events had been sampled. This is in agreement with previous theoretical, laboratory and field based studies (Stevens and Hornung 1988; 1990, Emmett *et al.*, 1991a,b); all have indicated that rapid re-vegetation of harvested areas is a major factor in reducing the duration of the nitrate leaching pulse.

In the case of the more alkaline situations (ie. higher weathering regimes) the increased biological activity associated with nitrate generation may even promote ANC production due to the increase in carbon dioxide induced weathering. Indeed, simple calculations based on alkalinity and pH measurements (cf. Neal *et al.*, 1997c) indicate that the higher alkalinity waters have carbon dioxide pressures two to ten times atmospheric levels. While this is relatively low for upland soil and groundwater situations, stream values should be, and usually are, close to equilibrium with the atmosphere due to the high degree of degassing (Neal *et al.*, 1997c,d). This weathering aspect may be of wider importance to acidification studies in that often the rate of weathering is taken as being constant, which, as some recognise (Sverdrup, 1996), it clearly need not be.

Following felling, there is often a fine balance between nitrate generation leading to increased stream acidification and reduction in strong acid anions (and possibly increased base cation concentrations due to enhanced weathering associated with carbon dioxide production) leading to reduced stream acidification (Neal *et al.*, 1998); and when set against other temporal variations in water quality, the net effect is often hard to discern. Indeed, if the average data for the survey are examined, it appears that the felled areas have a higher ANC than the forested sites: ie. on average, acidity is reduced following felling (standing forest ANC averages –40 μEq/l and clearfelled sites average –5 μEq/l: Table 4): these differences are not statistically significant because of the high variability. The average behaviour is nonetheless precisely what current acidification modelling predicts if the enhanced 'nitrate signal' and carbon dioxide driven weathering are not incorporated (Neal *et al.*, 1986). However, as with all aspects of this study, the heterogeneous nature of the catchments and the large range in chemical compositions makes quantitative evaluation difficult. For example, if the data are further subdivided with respect to time since felling and the influence of the extreme values is eliminated by using medians, then the following result is observed: ANC for standing forest, the first three years post-felling (when nitrate extremes are observed) and greater than three years since felling, give median values and standard deviations (in brackets) of –42 (41), –19 (107) and –35 (74) μEq/l, respectively: none of the medians can be considered as statistically significant yet, if these differences are actually representative, one must view hydrochemical response in a different way: put bluntly, for all the hydrochemical processes bar nitrate production, the major effect of conifer harvesting is to increase alkalinity and ANC. This type of information also raises many fundamental questions: these include: How many samples are required to provide a thorough representation of the spatial variability across catchments and regions? How can one capture the significance of all the interacting chemical and physical processes at a representative level of scaling? How can the nitrogen signal with felling be minimised to ensure harvesting leads to an improvement in water quality?

Conclusions

The opportunistic surveys of high and low flows across a range of forested and harvested sites have provided new insights into the effects of forestry practice on stream water quality under a range of flow extremes. The work shows the value of an organised campaign for opportunistic sampling using an infrastructure of enthusiastic staff from a regionally dispersed organisation associated with environmental matters (in this case the forestry industry). Indeed, the authors are aware of no other practical and fundable strategy for this type of endeavour. The approach is interactive in that field experience and insight of practising foresters is brought to bear on a scientific study while at the same time, the scientific issues are translated back to practical forestry management in an 'easily digestible form' for non specialists.

The results of this study, when combined with the Plynlimon findings (Neal, 1997e) show that the systems under study are highly heterogeneous in their chemical reactivities and water flow pathways. Further, for all the soil types, groundwater can provide an important component of acid neutralization. However, the extent of the chemical reactivity and water flow routing can be gauged only by direct measurement of stream chemistry owing to the apparently random nature of the variability. Indeed, the concept of there being 'representative catchments' with predicable runoff chemistry for particular combinations of geology, soil and landuse may at best prove elusive and may not even exist . This complexity makes process based field and computer based modelling studies of these upland environments at best difficult even without the added constraints of other factors such as forestry, climate and atmospheric pollution which can affect soil and groundwater quality.

The water quality of drainage from forested catchment areas can clearly deteriorate with felling; as the multiple regression analysis demonstrates a statistically significant positive link between concentrations of nitrate and aluminium and a negative link with ANC. Indeed, the only significant component generating enhanced acid runoff is nitrate; with felling the other strong acid anions show declining concentrations. Therefore, at a qualitative level, the primary area to address in terms of minimising acidification impacts due to deforestation or indeed to reduce stream acidification is to minimize nitrate production and/or maximize nitrate uptake within the catchment for the first few years after felling. Owing to the difficulties of within-stream removal of nitrate, mitigating strategies must focus primarily on management techniques to (a) reintroduce vegetation as soon as is convenient after felling, (b) to time felling such that nitrate build up is minimised and (c) to target management effort on the soils

where nitrate generation can be high. Many of these aspects are covered within current UK Forests and Water Guidelines (FC, 1993). However, the effects will be very variable from site to site in linkage with the extent of nitrate production within the first few years of felling, the nature of groundwater supplies and the relative effects of cation exchange and weathering processes. We highlight the difficulty in estimating nitrate production for individual soils and point, especially, to a lack of process and monitoring information on the brown earth soils whose high productivity can sometimes lead to particularly high nitrate production with felling.

Despite all the variability and lack of detailed process knowledge, it is clear that in many cases drainage water quality will not be affected significantly by felling and that without the nitrate pulse with felling, stream water quality will improve. At larger catchment scales which are more likely to be of concern to environmental managers (i.e. greater than 50 ha: over ten times the size of the survey catchments), local variability could easily be averaged out provided that there is adequate mixing upstream of the areas of environmental concern (to avoid localised inhomogeneities in water quality). With the current emphasis in Forests and Water Guidelines (FC, 1993) on phased harvesting within catchments, the impacts will be diluted even further. Indeed, current forestry guidelines which ensure good site management and a more 'landscape approach' to commercial forestry (FC, 1993, 1994) can clearly overcome or minimise harvesting impacts on water quality. Nonetheless, nitrate generation linked to acidification and aluminium generation could cause a problem for local drinking water supplies as aluminium concentrations exceeding 2 mg/l (222 μEq/l) have been observed (cf. Lewis, 1989). However, less than 25% of the sites have highly acidic waters (ANCs < –100 μEq/l) and only about 10% of the sites have aluminium concentrations over 100 μEq/l; about 30% of the sites register positive ANCs. There are, therefore, only a limited number of sites where such deterioration in water quality might arise. Further, there may well be local forestry management options to eliminate or greatly reduce even these extreme harvesting impacts. Indeed, more detailed analysis of the variability in the data may well identify those areas within catchments which are most vulnerable to change as well as revealing the most successful management techniques used to date in Wales.

The highly variable nature of the underlying processes at the catchment and landscape scales has meant that in the analysis of these data we have had to move away from the current trend of using catchment characteristics and broad critical loads approaches to assess regional water quality variation and land-use/atmospheric-pollution impacts. Indeed, from the work presented here and from comparison studies (Neal et al. 1997b, 1998) we question the basic validity and environmental management efficacy of the catchment characteristic and critical loads approaches. Consequently, there remains a need to monitor water chemistry under both high and low flow conditions to determine the actual state of water quality across a region. For future monitoring programmes, we strongly recommend the scheme used here as both relevant and cost effective at a range of scales.

Appendices

Appendix 1a. Site descriptions: locations

FE location	IH site code	Easting	Northing	FE Region	years since fell
BB64	B64	24840	23240	1	8
BB65	B65	24940	23150	1	7
BB66	B66	24890	23200	1	0
CA49	A49	26553	24910	2	1
CA50	A50	27790	27620	2	8
CA51	A51	27808	27580	2	4
CA52	A52	27710	27670	2	5
CA53	A53	27640	27668	2	0
CA57	A57	27745	26377	2	7
CA58	A58	27820	26195	2	0
CA59	A59	27250	29220	2	7
CA67	A67	27845	26265	2	0
CB54	B54	28000	27890	2	2
CB55	B55	27990	28004	2	0
CB56	B56	28048	28010	2	NA
DA18	A18	27900	33950	3	NA

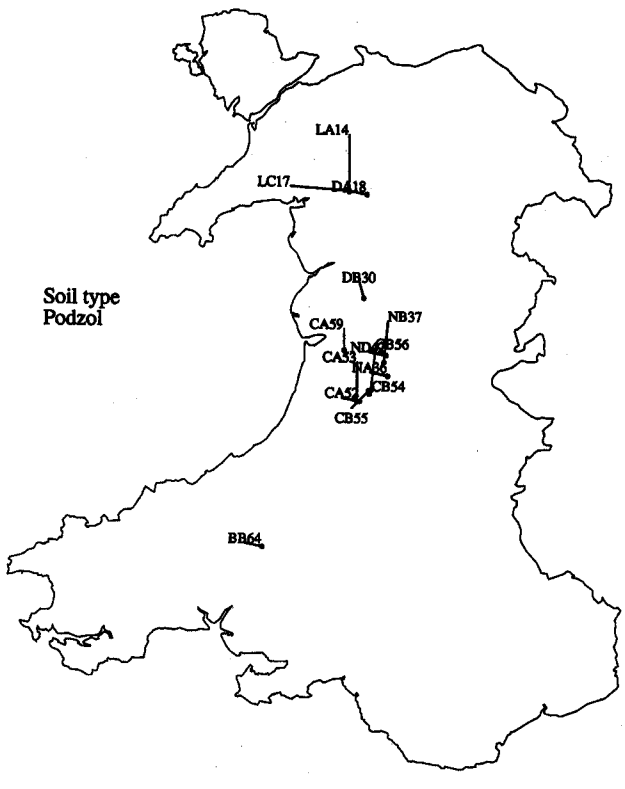
FE location	IH site code	Easting	Northing	FE Region	years since fell
DA20	A20	26777	33057	3	5
DA21	A21	26753	33080	3	5
DA22	A22	26772	33080	3	5
DA23	A23	26777	33080	3	4
DA24	A24	26813	33075	3	4
DA25	A25	28465	22333	3	5
DA27	A27	28346	31210	3	3
DA28	A28	28365	31195	3	1
DA29	A29	27670	30725	3	4
DA33	A33	27168	30180	3	0
DB19	B19	27740	32800	3	7
DB26	B26	28275	32085	3	15
DB30	B30	27820	30805	3	0
DB60	B60	28290	32115	3	2
DB61	B61	28315	32115	3	0
DB62	B62	28310	32120	3	0
DB63	B63	27870	30838	3	2
DC31	C31	27925	30815	3	9
DD32	D32	28005	30730	3	2
LA1	A1	25503	35103	4	3
LA10	A10	27975	34895	4	3
LA11	A11	27941	34785	4	0
LA13	A13	27376	34037	4	7
LA14	A14	27366	34033	4	7
LA15	A15	25500	25100	4	NA
LA16	A16	25500	25100	4	NA
LA17	A17	25500	25100	4	NA
LA2	A2	25520	305078	4	0
LA7	A7	27948	34825	4	3
LA8	A8	27985	34840	4	1
LA9	A9	27993	34868	4	1
LB12	B12	27758	35083	4	4
LB15	B15	27189	34028	4	3
LB16	B16	27248	34017	4	45
LB3	B3	25607	34848	4	3
LB4	B4	25586	34841	4	3
LB5	B5	25632	34800	4	0
LB6	B6	25623	34803	4	0
LC17	C17	27238	34078	4	8
NA34	A34	28550	28450	5	5
NA35	A35	28570	28390	5	3
NA36	A36	28550	28450	5	0
NA47	A47	30400	28150	5	1
NA48	A48	31470	28665	5	3
NB37	B37	28440	28860	5	2
NB38	B38	28490	28860	5	1
NB39	B39	28500	28840	5	2
NB40	B40	28495	28870	5	2
NC41	C41	28587	28950	5	1
ND42	D42	28500	29070	5	2
ND43	D43	28475	29120	5	7
NE44	E44	28520	29190	5	14
NE45	E45	28500	29205	5	1

Appendix 1b. Site descriptions:attribute; C represents control standing forest, SS = Sitka spruce, JL = Japanese larch, SP = Scots pine, NS = Norway spruce, WH = Western Hemlock, LP = Lodgepole pine, NF = Noble fir, NA = no information available.

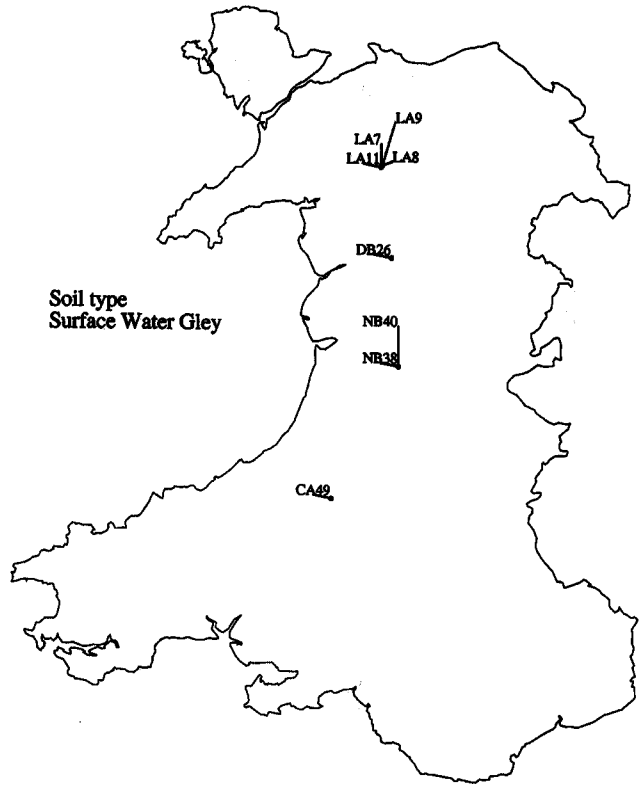
FE location	initial planting	species	soil	year felled	year of second planting
BB64	1942	SS	IIP	1988	1989
BB65	1942	SS	PG	1988	1989
BB66	1950	JL	PG	C	C
CA49	1959	SS	SWG	1994	NA
CA50	NA	SS	PG	1988	1988
CA51	1949	SS	PG	1993	1995
CA52	NA	SS	PIP	1992	1994
CA53	1942	SP	PIP	C	C
CA57	NA	NA	PG	1990	1992
CA58	1961	SS	B	C	C
CA59	1931	SS	IIP	1989	1989
CA67	1961	SS	B	C	C
CB54	1935	SS	PIP	1995	NA
CB55	1940	SS	PIP	C	C
CB56	1944	SS	PIP	NA	NA
DA18	1961	SS	IIP	NA	1993
DA20	1957	SS	PG	1992	NA
DA21	1951	SS	B	1992	1994
DA22	1951	SS	B	1992	1994
DA23	1951	SS	B	1992	1994
DA24	1949	SS	PG	1993	1996
DA25	1948	SS	PG	1992	1995
DA27	1929	JL	BE	1994	NA
DA28	1929	JL	BE	1994	NA
DA29	1938	SS	BE	1993	1995
DA33	1955	SS	BE	C	C
DB19	1935	SS	PG	1989	1991
DB26	1950	SS	SWG	NA	1981
DB30	1935	NLS	IIP	C	C
DB60	1950	SS	PG	1994	1997
DB61	1950	NS	PG	C	C
DB62	1950	SS	PG	C	C
DB63	1969	WH	BE	1995	1997
DC31	1935	NS	BE	NA	1988
DD32	1932	NS	BE	1993	1995
LA1	1936	SS	PG	1994	1995
LA10	1941	SS	PG	1994	1994
LA11	1947	SS	SWG	C	C
LA13	1939	WH	PG	1990	1991
LA14	1939	WH	PIP	1990	1991
LA15	1936	SS	PIP	1994	NA
LA16	1936	SS	PIP	1950	NA
LA17	1936	SS	PIP	1988	NA
LA2	1936	SS	PG	C	C
LA7	1942	NS	SWG	1994	1995
LA8	1942	SS	SWG	1994	1994
LA9	1942	SS	SWG	1994	NA
LB12	1937	NS	PG	1993	1993
LB15	1929	NS	PG	1994	NA
LB16	1939	LP	PG	1950	1951

Appendix 1b. cont.

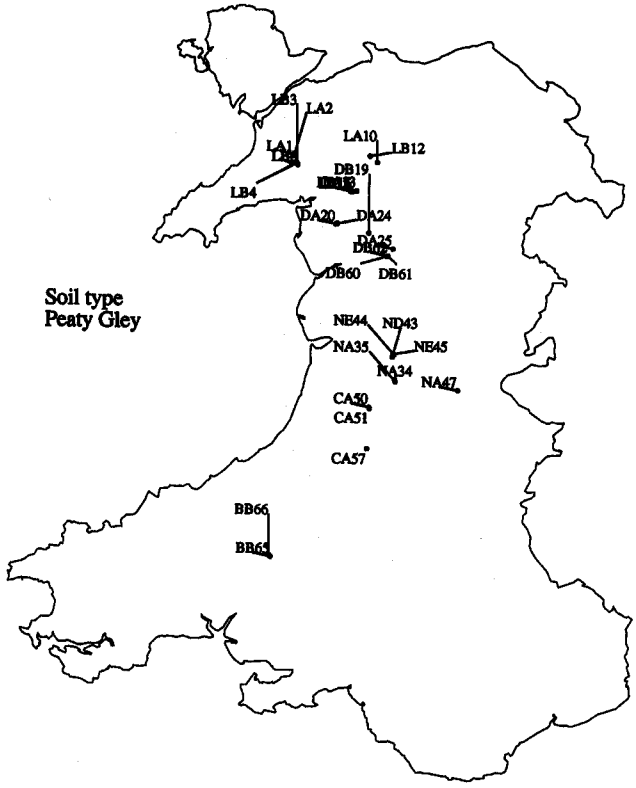
FE location	initial planting	species	soil	year felled	year of second planting
LB3	1946	SS	PG	1994	1995
LB4	1946	SS	PG	1994	NA
LB5	1942	SS	PG	C	C
LB6	1942	SS	PG	C	C
LC17	1914	NS	IIP	1988	1989
NA34	1940	SS	PG	1992	1994
NA35	1940	SS	PG	1992	1994
NA36	1947	SS	IIP	C	C
NA47	1960	SS	PG	1995	1997
NA48	1955	NF	BE	1994	1997
NB37	1948	SS	IIP	1994	1996
NB38	1951	SS	SWG	1994	1996
NB39	1951	LP	BE	1994	1996
NB40	1951	SS	SWG	1994	1996
NC41	1952	SS	BE	1995	1997
ND42	1947	SS	IIP	1995	1996
ND43	1947	SS	PG	1990	1995
NE44	1954	SS	PG	1983	1993
NE45	1954	SS	PG	1996	NA



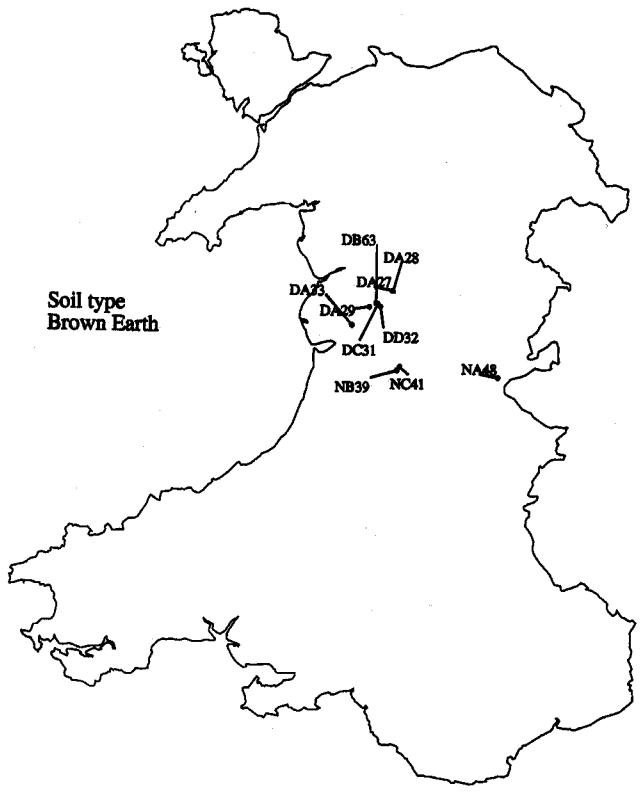
Appendix 2a. The location and sample identification of podzol sampling sites across Wales.



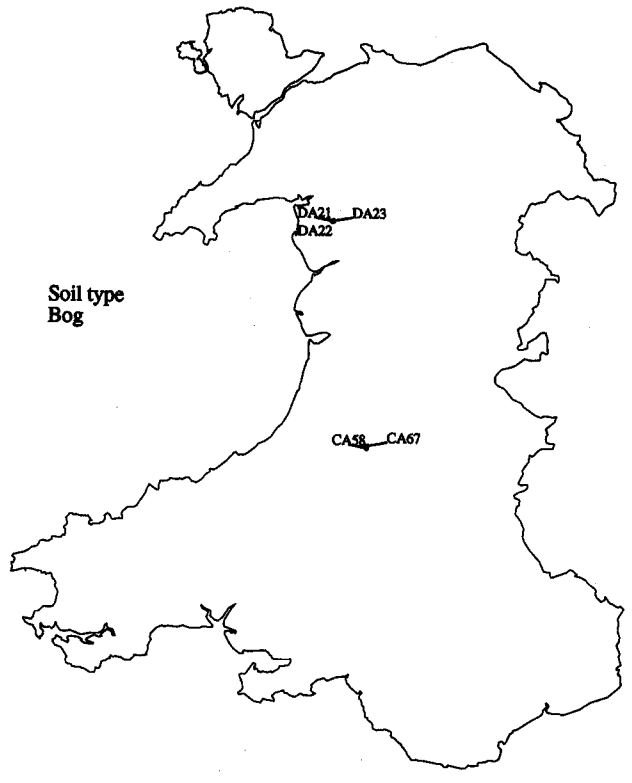
Appendix 2b. The location and sample identification of surface water gley sampling sites across Wales.



Appendix 2c. The location and sample identification of peaty gley earth sampling sites across Wales.



Appendix 2d. The location and sample identification of brown earth sampling sites across Wales.



Appendix 2c. The location and sample identification of bog earth sampling sites across Wales.

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We are indebted to the enthusiastic help of Bob Farmer with the design and implementation of the programme and to FE field staff with the sampling programme. We are also indebted to reviews by Tom Nisbet (FA) and Graham Rutt (EA) as well as external and other reviewers for their first class critical assessment of the work, which allowed a far better and balanced contribution to be produced.

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Appendix 3a. **A summary of the water quality across the 67 sampling sites at baseflow.**

	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	SO_4 mg/l	Mn µg/l	Fe µg/l
Median	4.95	0.23	1.57	0.91	6.24	50.95	24.40
Min	3.01	0.06	0.41	0.54	2.72	0	0.9
Max	10.46	0.94	12.26	2.83	15.68	433.4	586.9
	Li µg/l	**Be µg/l**	**B µg/l**	**Al µg/l**	**Sc µg/l**	**Cr µg/l**	**Ni µg/l**
Median	1.02	0.09	6.19	140.45	0.55	0.10	1.41
min	0.03	0.02	3.17	9.08	0.06	0.00	0.14
max	3.06	0.54	12.46	1366.63	1.91	0.45	7.99
	Co µg/l	**Cu µg/l**	**Zn µg/l**	**Rb µg/l**	**Sr µg/l**	**Y µg/l**	**Mo µg/l**
Median	0.38	1.74	11.29	0.27	5.89	0.32	0.20
min	0.03	0.32	2.31	0.07	2.86	0.03	0.00
max	6.07	10.19	1840.36	1.50	46.24	2.76	14.71
	Cd µg/l	**Sb µg/l**	**Cs µg/l**	**Ba µg/l**	**La µg/l**	**Ce µg/l**	**Pr µg/l**
Median	0.06	0.04	0.02	4.81	0.15	0.26	0.04
min	0.00	0.00	0.00	1.37	0.02	0.02	0.00
max	5.63	1.41	4.83	72.57	2.88	13.36	0.74
	Pb µg/l	**Th µg/l**	**U µg/l**	**Si mg/l**	**DOC mg/l**	**NO_3 mg/l**	**NH_4 mg/l**
Median	0.34	0.01	0.01	1.23	1.50	1.38	0.02
min	0.01	0.00	0.00	0.25	0.00	0.00	0.00
max	67.77	0.19	0.08	4.40	9.90	19.25	0.13
	SRP mg/l	**F mg/l**	**Cl mg/l**	**Br µg/l**	**I µg/l**		
Median	0.04	0.05	8.40	33.50	1.40		
min	0.00	0.00	4.20	15.00	0.30		
max	0.19	0.09	17.70	65.00	3.80		
	pH	**G-alk1 µEq/l**	**G-alk2 µEq/l**		**ANC µEq/l**	**ANCcb µEq/l**	
Median	5.17	0.60	−4.60		−21.42	−7.55	
min	4.30	−45.31	−40.03		−167.68	−152.87	
max	7.13	465.08	468.03		464.66	444.66	

Appendix 3b. A summary of the water quality across the 67 sampling sites at stormflow.

	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	SO_4 mg/l	Mn µg/l	Fe µg/l
Median	4.76	0.24	1.46	0.90	6.18	63.50	40.90
Min	2.65	0.00	0.43	0.34	2.57	0.20	0.00
Max	8.73	1.95	29.20	5.79	20.96	529.50	1549.90

	Li µg/l	Be µg/l	B µg/l	Al µg/l	Sc µg/l	Cr µg/l	Ni µg/l
Median	1.11	0.12	5.53	192.67	0.39	0.13	1.67
Min	0.04	0.01	0.00	8.29	0.06	0.00	0.13
Max	3.04	0.58	11.76	1135.09	1.66	10.80	13.10

	Co µg/l	Cu µg/l	Zn µg/l	Rb µg/l	Sr µg/l	Y µg/l	Mo µg/l
Median	0.63	1.81	12.33	0.29	5.80	0.33	0.36
Min	0.02	0.57	2.01	0.01	2.27	0.03	0.00
Max	37.42	8.24	866.56	1.71	101.38	2.87	11.23

	Cd µg/l	Sb µg/l	Cs µg/l	Ba µg/l	La µg/l	Ce µg/l	Pr µg/l
Median	0.07	0.06	0.02	5.04	0.19	0.27	0.03
Min	0.00	0.00	0.00	1.24	0.01	0.01	0.00
Max	2.74	0.98	88.40	87.71	3.32	10.75	0.59

	Pb µg/l	Th µg/l	U µg/l	Si mg/l	DOC mg/l	NO_3 mg/l	NH_4 mg/l
Median	0.47	0.01	0.01	1.25	2.00	1.53	0.02
Min	0.01	0.00	0.00	0.20	0.00	0.00	0.00
Max	64.79	0.14	0.16	4.50	14.70	18.50	0.23

	SRP mg/l	F mg/l	Cl mg/l	Br µg/l	I µg/l
Median	0.04	0.05	7.90	38.00	1.60
Min	0.00	0.00	3.80	10.00	0.30
Max	0.35	0.19	16.80	92.00	7.60

	pH	G-alk1 µEq/l	G-alk2 µEq/l	ANC µEq/l	ANCcb µEq/l
Median	5.06	–0.44	–1.26	–25.40	–14.58
Min	4.04	–90.45	–89.69	–132.06	–198.14
Max	7.18	1499.83	1506.76	1496.11	1500.60

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